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Porous polymer magnetic adsorbents for dye wastewater treatment

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Abstract: The recent decade has witnessed adsorption technology emerging as an advanced dye wastewater treatment method with great potential and a grand blueprint, in which the specific surface area and active sites of the adsorbent are considered to be the two most important characteristics largely impacting the adsorption performance. Therefore, two kinds of magnetic porous adsorbents (HSF and HSVF) with different specific surface areas and activity sites were fabricated. Both of them exhibit excellent performance with remarkable adsorption capacities for negative dye Sunset yellow (SY). Furthermore, their adsorption kinetic and isotherm were further studied and
compared in detail. The results revealed that introducing strong active sites could improve the adsorption capacity and rate effectively even though sacrificing part of specific surface areas, indicating that active sites might play a dominant role during the dye adsorption process. Multiple interactions introduced by the pyridine functional group in the sample HSVF also showed synergistic effects. In addition, the adsorbents could be recycled rapidly by magnetism, which exhibited the advantages of easy-operation.

Graphical Abstracts:

Keywords: magnetic hybrid adsorbent, hypercrosslinked polymer, dye, adsorption, active sites, specific surface areas

1. Introduction
Nowadays, water pollution has attracted great attention worldwide due to the high toxicity of contaminants (Karaouzas et al., 2021; Nakamura, 2010, 430; H. Xie et al., 2020) and the booming variety of the them with the development of industry, such as spilling oil (Jin et al., 2019) heavy metal ions (Roy et al., 2020) antibiotics (Linye Zhang et al., 2019, 39) and dyes (Yadav et al., 2021) Among them, organic dye wastewater discharged from the textile and food industry has led to serious health and environmental crisis (Lv et al., 2019; Z. Zhang et al., 2020) In order to treat dye-polluted wastewater efficiently, lots of treatment technologies have been developed, including chemical flocculation, membrane separation, photocatalysis, and adsorption (Xi Quan Cheng et al., 2018, 258; Pavithra et al., 2019, 1; Verma et al., 2012; Y. Wu et al., 2022) among which the adsorption technologies have become very popular due to their low-cost, convenient and easy-operation.

Adsorbent is the core of adsorption technology. Different compositions and structures of adsorbents could generate different interactions with dye during the adsorption process, such as Van der Waals’ force, electrostatic interaction, π-π interaction, and so on (Y. Zhou et al., 2019) thus impacting the adsorption performance. In general, specific surface areas and activity sites of adsorbents are considered as the critical structural and compositional properties that have a great influence on adsorption behavior (Castaldo et al., 2021, 129463) Therefore, many inorganic porous materials were chosen because of their intrinsic high specific surface areas and abundant activity sites (B. Cheng et al., 2011; Lie Wang et al., 2014, 348; Zhu et al., 2016, 239) In recent years, organic porous materials were drawn to attention in the adsorption field (Su et
Hypercrosslinked polystyrene (HCP) was the most common organic porous material and received much attention in the adsorption field due to its remarkable structure and functional designability. Recently, HCP with different structures was prepared, such as Core-Shell, Yolk-Shell and polymer brush. These structures with different specific surface areas displayed different adsorption performances further. In addition to the influence of specific surface areas on adsorption, another key factor is how the active sites affect adsorption performance. Introducing active sites could generate different interactions between adsorbents and adsorbates. Styrene had a robust copolymerization ability so that HCP could be modified by diverse functional monomers. The previous researches have proved that high specific surface areas and strong interactions were beneficial for improving adsorption performance. However, in most cases, high specific surface areas and strong active sites were not available simultaneously for HCP because the functional modification often result in the decrease of the specific surface areas. Therefore, it is necessary for designing adsorbents to discuss the influence degree of specific surface areas and active sites on adsorption performance. In addition to the adsorption performance, recycling adsorbents was another noteworthy challenge for adsorption technology. Hybrid of Fe$_3$O$_4$/HCP could be an effective and facile method to recycle
adsorbents fleetly by magnetism. (Chen et al., 2020; Essandoh et al., 2020; M. Zhang et al., 2013)

Herein, two kinds of magnetic porous Fe$_3$O$_4$/HCP hybrid microparticles (HSF and HSVF) with different specific surface areas and active sites were obtained by mature miniemulsion polymerization and Friedel-Crafts reaction. After that, Sunset yellow (SY) which may cause lots of health crises was regarded as a model dye (Coros et al., 2020) to explore their different adsorption performances and mechanisms affected by specific surface areas and active sites. The result revealed that both adsorption rates and capacity could be improved observably after introducing 10% of molar fraction of strong positive active sites even though about 30% specific surface areas were sacrificed. So, it could be concluded that active sites played a dominant role during the dye adsorption process. What’s more, the adsorbents could generate nice adsorption performances for cationic and anionic dye simultaneously due to the multifarious interactions with dye molecules. Meanwhile, the adsorbent could be recycled by magnetism, which certified that it was an effective method to enhance the practicability of HCP.

2. Materials and methods

2.1. Materials

Styrene (St), 4-vinylpyridine (4VP), divinylbenzene (DVB), sodium dodecyl sulfate (SDS), anhydrous ferric chloride (FeCl$_3$), ferrous sulfate heptahydrate (FeSO$_4$·7H$_2$O), Rhodamine B (RhB) and Methyl blue (MB) were purchased from Aladdin Biochemistry Co. Ltd. St, 4VP and DVB were filtered through the alkaline alumina
column to remove the inhibitor for further use. Potassium persulfate (KPS) was purchased from Meryer Co. Ltd. and was recrystallized from water. 1,2-dichloroethane (DCE), ammonia (NH₃•H₂O), oleic acid (OA), dimethoxymethane (FDA) and N-hexadecane (HD) were purchased from Macklin Co. Ltd. and DCE was dried over CaH₂ and distilled before use. Sunset yellow (SY) was purchased from Beijing Warwick Chemical Co. Ltd. Except for the indication, other reagents were used without further purification.

2.2. Synthesis of porous adsorbent

Firstly, OA-coated Fe₃O₄ (OA-Fe₃O₄) nanoparticle was synthesized by a facile coprecipitation method (the details were given in the supporting information). Then the hybrid microparticle was prepared through miniemulsion polymerization. OA-Fe₃O₄ (1.5 g) was separated from water by magnet and redispersed into a mixture of St (5 g, 48.1 mmol), DVB (0.5 g) and HD (0.15 g) under ultrasonication as the oil phase of the following miniemulsion polymerization. SDS (0.25 g) was dissolved in water (50 mL) as the water phase. Then the oil phase was added dropwise to the water phase under mechanical stirring (500 rpm) for 30 min to form raw emulsion. After that, the system was homogenized by ultrasonication under ice-cooling for 20 min at 225 W. The obtained emulsion was heated to 70°C, and KPS (0.05 g) was dissolved in 10 mL water then joined to initiate the reaction. After 24 h, the hybrid microparticle (named SF) was collected by centrifugation at 8000 rpm for 15 min. For the functional microparticle (named SVF), 0.5 g of St (4.81 mmol) was replaced with 0.5 g of 4VP (4.76 mmol), then the same reaction was conducted. The target product, Fe₃O₄ incorporated magnetic
microparticles could be collected and purified by magnetism, thus the polymeric by-
product, microparticles without Fe$_3$O$_4$, could be removed conveniently.

The hypercrosslinked network was conducted referring to the previous literature.(B.
Li et al., 2013; Q. Li et al., 2016) The details were as the followings: SF or SVF (0.5 g)
was dispersed in DCE (20 mL) for 5 h to swell adequately under N$_2$ atmosphere, then
FDA (2 mL) and FeCl$_3$ (3.65 g) were added into the mixture at 45°C for 5 h. Next, the
Friedel-Crafts reaction was heated at 80°C for 19 h. The resulting porous adsorbent was
filtered and washed with methanol. After being washed in a Soxhlet with methanol for
24 h, the adsorbent was dried in a vacuum oven at 60°C for 24 h. The obtained materials
are denoted as HSF and HSVF, the preparation procedures and the schematic structure
of adsorbents were illustrated in the supporting information Scheme S1.

2.3. Characterization

The structure data of Fe$_3$O$_4$ was recorded by X-ray diffraction (XRD, 
D/max2550VB/PC). Fourier transform infrared (FT-IR) spectra were investigated by a
Nicolet FTIR 5700 spectrometer. The morphology of the hybrid microparticle was
observed by Transmission Electron Microscope (TEM, JEOL JEM-2100).

Hydrodynamic diameter ($D_h$) obtained via Dynamic Light Scattering (DLS) and Zeta
potential of adsorbents were measured on Malvern Zetasizer Nano ZS90. The specific
surface area and porous structure of adsorbents were measured by nitrogen adsorption-desorption analysis (Micromeritics ASAP2460). The chemical composition of the SY
and adsorbents after adsorption were obtained by X-ray photoelectron spectroscopy
(Thermo Scientific ESCALAB 250Xi).
2.4. Batch adsorption experiments

The batch adsorption experiments were conducted in a constant temperature rocker rotator at different concentrations, time, temperatures, and pH, the solid-to-liquid ratio was 1 g/L. The concentrations of the dye solutions after adsorption were determined by UV-vis spectrophotometer (UV-2450/2550, Shimadzu). Then the adsorption capacity was calculated by the following equations:

$$q_t = \frac{(C_0-C_t) \times V}{m}$$  \hspace{1cm} (1)

$$q_e = \frac{(C_0-C_e) \times V}{m}$$  \hspace{1cm} (2)

$$RE = \frac{C_0-C_e}{C_0} \times 100\%$$  \hspace{1cm} (3)

$$q_d = \frac{C_d \times V}{m}$$  \hspace{1cm} (4)

$$DE = \frac{q_d}{q_e} \times 100\%$$  \hspace{1cm} (5)

$$q_r = q_e - q_d$$  \hspace{1cm} (6)

Where $C_0$ (mg/L), $C_t$ (mg/L), $C_e$ (mg/L), $C_d$ (mg/L) were the initial, time $t$, equilibrium, and desorption concentrations of SY solutions, respectively. $q_t$ (mg/g) and $q_e$ (mg/g) represent the adsorption capacity at time $t$ and equilibrium. $V$ and $m$ were the volume of dye solution and mass of adsorbent. $RE$ (%) was the dye removal efficiency. $q_d$ (mg/g) was the desorption capacity of each recycle. $DE$ (%) represents the desorption efficiency and $q_r$ (mg/g) was the residual adsorption capacity after desorption each time.

Adsorption selectivity experiments were conducted at 298 K, pH = 2, the mixing dye solutions were prepared by mixing the same volume of 200 mg/L a single dye solution. According to the batch adsorption experiments, the adsorption kinetics, isotherms and adsorption mechanisms were investigated further.
3. Results and discussion

3.1. Synthesis and characterization of adsorbents

The Fe$_3$O$_4$ nanoparticle was prepared and modified by OA successfully (Figure S1). As for the hybrid microparticle, obvious cladding structures have appeared (Figure 1a, 1b and Figure S2), and the hydrodynamic diameter of the hybrid microparticle was about 78.8 nm measured by DLS. Further, according to the FT-IR spectrogram (Figure 1c), the peaks at 2923 cm$^{-1}$ and 3024 cm$^{-1}$ were from stretching vibration of saturated and unsaturated C-H respectively, which demonstrated the successful preparation of SF. Besides, the characteristic peak at 1412 cm$^{-1}$ was observed on the curve of SVF on account of the stretching vibration of C=N bond from the pyridine ring.

Zeta potentials of these two adsorbents were researched (Figure 1d). The general trend of the potentials of both HSF and HSVF were decreased with the increase of pH values. The Zeta potentials were positive at low pH and dropped to negative at higher pH values. When pH = 2, H$^+$ was adsorbed on the surface of HSF easily in such strong acid aqueous, therefore, HSF showed a positive value (8.12 mV). With the increase of pH value, the concentration of H$^+$ decreased, and when the aqueous solution became basic, the surface of HSF was occupied by more OH$^-$, resulting in its potential decrease. As for HSVF, in addition to the adsorption of H$^+$ on the surface, its pyridine structure could be protonated, leading to much higher positive potential than that of HSF at pH = 2. This also resulted in the higher potential values of HSVF than that of HSF at each
pH across the entire pH range. When the pH value increased, deprotonation of pyridine ring also contributed to the decrease of the potential.

For adsorbents, their specific surface area and porous structure were studied by N\textsubscript{2} adsorption-desorption analysis (Figure 1e). From the curves, before hypercrosslinking, SF did not present the capacity of N\textsubscript{2} adsorption, while HSF had rapid N\textsubscript{2} adsorption at low relative pressure which demonstrated the existence of micropores in HSF. Furthermore, obvious hysteresis loops appeared on the curves of HSVF, but the hysteresis loops of HSF were almost suppressed revealing that adsorbent HSVF had a more mesoporous structure. According to Figure 1f and 1g, the pores in HSF were micropores mainly, but there were more mesopores and macropores in HSVF so its specific surface area decreased by about 30\% compared with that of HSF after substituting 10\% molar fraction of St with 4VP.

**Figure 1.** (a, b) TEM images and hydrodynamic diameter (measured by DLS) of (a) SF and (b) SVF, (c) the FT-IR spectra of SF and SVF, (d) Zeta potentials of HSF and
HSVF, (e) N₂ adsorption and desorption curves of SF, HSF and HSVF, (f, g) the pore size curves of (f) HSF and (g) HSVF.

When part of St was replaced by 4VP, the reactive sites were reduced for Friedel-Crafts reaction due to the strong polarity of the pyridine rings. In addition, the introduction of the pyridine rings to the molecular chain resulted in the increase of the distance between the benzene rings, so it was more difficult for HSVF to form micropores than HSF. The detailed information about the specific surface areas was listed in Table 3.1.

Table 3.1 Summary of the specific surface area of HSVF and HSF

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$S_{\text{BET}}^a$</th>
<th>$S_m^b$</th>
<th>$PV^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m²/g</td>
<td>m²/g</td>
<td>cm³/g</td>
</tr>
<tr>
<td>HSF</td>
<td>685.95</td>
<td>343.43</td>
<td>1.0058</td>
</tr>
<tr>
<td>HSVF</td>
<td>471.88</td>
<td>201.42</td>
<td>0.4593</td>
</tr>
</tbody>
</table>

*a BET specific surface area of adsorbents; *b t-plot micropore area of adsorbents; *c Pore volume calculated from the nitrogen isotherm.

3.2. Adsorption behavior of HSF and HSVF

The whole adsorption process was present in Figure 2a. On account of the existence of Fe₃O₄, the extra merits clearly that the adsorbent could be facilely recycled by magnetic separation to avoid secondary pollution. There were lots of factors to affect the adsorption behavior of adsorbents. Firstly, pH had a great influence on adsorption. Figure 2b indicated that the adsorption capacity of these two adsorbents was reduced by the increase of pH values. This was because SY was a kind of anionic dye (its composition and structure were illustrated in Figure S3), its negative potential would
make it diffuse into adsorbents easier because of positive surface potential of adsorbents in the strong acid environment. With the increase of pH, the nanoparticle surface potential transformed from positive to negative, thus electrostatic-interaction-caused dye diffusion would be limited by the resulting electrostatic repulsion, then the diffusion depended only on concentration gradient.

Furthermore, the effect of initial concentration on dye adsorption was studied (Figure 2c and 2d). For both of them, their adsorption capacity \( (q_e) \) enhanced with the increase of dye initial concentration and reached equilibrium at last. This could be explained that with the increase of initial concentration, a higher concentration gradient was generated and dye molecules could diffuse into the pores of adsorbent easier, therefore, the probability of adsorption was higher and the \( q_e \) could be improved. However, when all the adsorption sites were occupied entirely by dye molecules, the adsorption capacity reached equilibrium. As for HSVF, its removal efficiency for SY solution decreased with the increase of initial concentration because of a disproportionate increase in the SY concentration versus the adsorbed SY molecules. When concentration rose from 500 to 800 mg/L, adsorption capacity almost achieve equilibrium, increasing concentration constantly result in a decline in the removal efficiency.\(^\text{(Tang et al., 2021)}\)

Noticeably, the removal efficiency of HSF toward SY increased as the initial dye concentration rose from 100 to 200 mg/L, and then decreased at a higher initial concentration. It could be stated that the positive surface potential of HSF was not as strong as HSVF’s, so compared to HSVF, the SY molecule diffused into HSF relied on the concentration gradient mainly. Therefore, there were fewer SY molecules diffusing
into HSF than HSVF at 100 mg/L. In addition, HSF did not have the strong electrostatic attraction as the interaction between tertiary amine and sulfonate in HSVF, so the desorption could happen easier at low initial concentration for HSF. So, the too- low $q_e$ value resulted in the low removal efficiency for HSF at 100 mg/L.

**Figure 2.** (a) Photographs of adsorption and magnetic separation processes, (b) the influence of pH on adsorption capacity $q_e$, (c, d) the influence of dye solution initial concentration on (c) HSVF and (d) HSF adsorption capacity $q_e$ and removal efficiency $RE$.

To further confirm the electrostatic attraction between HSVF and SY, the two kinds of adsorbents after adsorption at pH = 2 were characterized by XPS. As shown in the Figure 3b, the N 1S peak belonging to azo structure of SY molecular was at 400.2eV, it also appeared in Figure. 3c and 3d. There was a peak at 402.3eV in HSVF which was attributed to the protonation of pyridine(Muglali et al., 2011) (Figure 3d), the strong
electrostatic attraction could generate between HSVF and SY, but there was no obvious change in HSF.

Figure 3. (a) XPS spectra of HSF and HSVF, (b) N 1s core-level spectra of SY, (c) HSF after adsorption, and (d) HSVF after adsorption.

3.3. Study of adsorption kinetic

Investigation of the kinetic process could provide lots of information about adsorption systems. HSVF and HSF were tested at initial concentrations 200 mg/L and 100 mg/L respectively. From Figure 4a and 4b, HSVF and HSF reached equilibrium in about 12 h and 6 h. Comparing to other nonporous adsorbents, their porous structure endows them higher adsorption capacity, thus their equilibrium time was always longer
than nonporous analogues. (Tang et al., 2021; Tran et al., 2017) Furthermore, pseudo-first-order-model (PFO) and pseudo-second-order-model (PSO) were used to fit the whole adsorption process and investigate the adsorption mechanism. In general, the adsorption process could be divided into three stages: (1) liquid film diffusion (external diffusion), (2) internal diffusion and (3) adsorption on active sites. Stage (3) occurring very quickly, so stages (2) and (3) could be regarded as occurred simultaneously. (J. Wang and Guo, 2020) The fitting results displayed that PSO was the better model for both of them, which indicated that there was chemisorption for HSVF and HSF during the adsorption processes. (Arabkhani and Asfaram, 2020)

Generally speaking, as long existed electron transfer or electron pair sharing in the adsorption process, it would be considered as chemisorption. (Tran et al., 2017) On the one hand, the pyridine structure in HSVF could be protonated and produce strong electrostatic attraction with the sulfonate of SY molecule, and hydrogen bond could be formed between the phenolic hydroxy of SY and pyridine group. (Urakawa and Yasue, 2019) Besides, $\pi-\pi$ stacking could be also generated in the hydrophobic skeleton. (Fada Li et al., 2021, 105018) On the other hand, a high chemical potential generated by electrostatic interaction and concentration gradient made diffusion easier, whether external diffusion or internal diffusion.

As for HSF, its aromatic group was electron-rich because of the C-C backbone and the aromatic group of SY was electron deficiency due to the strong polar group, so the main interaction between SY and HSF was only $\pi-\pi$ stacking. (Tran et al., 2017)
Therefore, the interactions between dyes and HSF were weaker than that between dyes
and HSVF.

Furthermore, the intra-particle diffusion model was used to investigate the different
stages of adsorption (Figure 4c and 4d). The detailed fitting data was listed in table S1.
The whole adsorption process could be divided into three stages. In the first stage, SY
molecules diffused through the liquid film; in the second stage, the dye molecules
diffused into the pores of adsorbent and produced the interaction with the active sites
at the same time, and in the last stage, the adsorption tended to equilibrium. During the
diffusion process, the \( K_p \) value of HSVF was always higher than HSF because of the
higher chemical potential. Besides, the pore diameter of HSVF was larger than HSF so
the influence of sterically hindered effect was reduced during the internal diffusion.
However, HSVF needed a longer equilibrium time than HSF because the relatively
sufficient adsorption sites needed to be occupied for adsorbate at higher initial
concentration.(Chen et al., 2020; Fila et al., 2022, 137245; Hao Zhang et al., 2022,
133604) When decreasing the initial concentration to 100 mg/L for HSVF (Figure S4),
its equilibrium time was shorter even though HSF had a higher specific surface area
which could provide more contact probability. This could be explained that HSVF had
a higher chemical potential for SY diffusion resulting from the strong electrostatic
interaction at the same initial concentration, meanwhile, adsorbates might be more
likely to be adsorbed on HSVF due to various of interactions. What’s more, the weak
interaction for HSF might lead to desorption easier because the whole adsorption was
a dynamic adsorption-desorption process.
Figure 4. (a, b) Adsorption kinetic curves of HSVF and HSF fitted with PFO (pseudo-first-order-model, red curves) and PSO (pseudo-second-order-model, azure dashed curves), and (c, d) intra-particle diffusion model of HSVF and HSF.

3.4. Study of adsorption isotherm

Adsorption isotherm was the relationship between $C_e$ and $q_e$ at a certain temperature. In this study, the isotherms of HSVF and HSF at 298 K, 308 K, 318 K were investigated respectively, and Freundlich, Langmuir, Temkin models were used to fit the isotherm dates, respectively. The detailed fitting dates were listed in table S2 and table S3. As was clearly observed in Figure 5a, 5b, and 5c, the Langmuir model had better fitting results than other two models for HSVF at each temperature. What’s more, the maximal
adsorption capacity of the Langmuir model was 343.90 mg/g, which was close to the experimental values ($q_e = 331.37$ mg/g). This declared that the adsorption on the HSVF was monolayer adsorption and active sites were distributed uniformly on the surface of HSVF. Meanwhile, the separation factors of Langmuir model $R_L$ values of each temperature were between 0~1, thereby, this process was a favorable adsorption. (Essandoh et al., 2020) Temkin models were suitable for HSF at each temperature and demonstrated that the chemical adsorption positively participated in the adsorption process. (Guo et al., 2014, 3081) This result was consistent with the kinetic experiment. In addition, the maximal adsorption capacity of HSVF (331.37 mg/g) was greater than HSF (203.92 mg/g) even though HSF had larger specific surface areas. It could be stated that strong interactions with adsorbates could provide better adsorption performances, because the strong interactions may make incorporation easier between adsorbents and adsorbates, and improve the adsorption capacity effectively even though high specific surface areas could supply more nanospace. (Fu et al., 2022, 8784; J. Wu et al., 2021)
Figure 5. Isothermal model fitting curves at different temperatures of (a ~ c) HSVF and (d ~ f) HSF.

3.5. Study of adsorption selectivity

Study of adsorption selectivity for different dye molecules was meaningful for understanding the adsorption mechanism. Therefore, the anionic SY solution was mixed with cationic Rhodamine B (RhB) and another anionic Methyl blue (MB) for separation testing respectively. In the SY/RhB mixed-dye solution (Figure 6a), not only the SY dye, but also the cationic RhB was removed effectively by HSVF simultaneously. It could be explained that adsorption of dye molecules by HSVF depends on various of interactions. Although there was no electrostatic attraction due to the same charge, the cationic RhB could be adsorbed by π-π stacking and hydrogen bond by HSVF. As for HSF, it could also generate adsorption capacity for anionic and cationic dye in the mixture solution, but the adsorption capacity for RhB was higher than it for SY obviously, the reason might be that the cationic dye molecules tend to
aggregate in the protic polar solvents, (Sarkar et al., 2008) therefore, the RhB was easy to be adsorbed in abundance. In Figure 6b, the molecular weight of dye didn’t have obvious influence on adsorption selectivity, the concentrations of SY and MB were decreased and the adsorption sites were occupied by SY and MB simultaneously, but the adsorption performance of HSVF was better than that of HSF. Therefore, it could be concluded that a nice adsorption performance for both cationic and anionic dye could be realized rely on various of interactions, while more interactions also provided better adsorption capacity. HSVF could be a promising adsorbent for the multifarious dye wastewater treatment with great potential.

Figure 6. (a) the UV-vis spectra of SY/RhB mixture solution before and after adsorption, (b) the UV-vis spectra of SY/MB mixture solution before and after adsorption.

3.6. Study of desorption mechanism

The desorption capacity of HSVF and HSF was investigated with 1 M NaOH as desorption solution. From Figure 7a, the desorption efficiency of HSVF was increased
gradually and tended to balance at last, but the HSF showed an opposite trend. This could be explained that the NaOH solution would change the surface potential of the adsorbent and destroy the interaction between adsorbent and SY molecules. The strong electrostatic attraction was the dominating interaction between HSVF and SY, it could be influenced greatly by NaOH, so the desorption efficiency of HSVF could reach 85.49% after serval times of desorption. As for HSF, there was no strong electrostatic attraction between HSF and SY. Therefore, less desorption of SY molecules could happen. This result reflected the different electrostatic interactions of HSVF and HSF with SY. What’s more, the balance residual adsorption capacities of HSVF and HSF (Figure 7b) were 5.21 mg/g and 10.76 mg/g respectively, this ratio was in accordance with their pore volume, so it could be inferred that the molecules which were hard to be desorbed were anchored in the pore of adsorbent by steric hindrance.

**Figure 7.** (a) Desorption efficiency of HSVF and HSF, (b) residual adsorption capacity of HSVF and HSF.

4. Conclusions
In this study, two kinds of magnetic adsorbates HSF and HSVF were synthesized facilely and both exhibited convenient recyclability. Further, their different adsorption performances caused by the different interactions between dyes and adsorbents were thoroughly studied. Both of them showed nice adsorption capacities for SY (203.92 mg/g and 331.37 mg/g), but there was an obvious improvement for HSVF because of the existence of stronger active sites even if it has a lower specific surface area. This reflected that the strong interactions between the active sites and dyes played a dominant role during the dye adsorption process. In addition, both HSVF and HSF showed universal adsorption performances for both anionic and cationic dyes. Furthermore, in the desorption experiments, the higher desorption efficiency of HSVF in NaOH aqueous solution proved that it had a strong electrostatic attraction, while more residual adsorption capacity of HSF, may result from its higher pore volume. Therefore, it could be concluded that stronger active sites could improve adsorption rates even with reduced specific surface area. In addition, introducing strong active sites was an effective method to improve adsorption capacity, strong active sites of adsorbent had a greater influence on adsorption capacity than specific surface areas. Meanwhile, various of interactions between adsorbents and dye molecules could generate nice adsorption performances for different kinds of dye simultaneously. This research conduces to understand the adsorption process in porous adsorbent system, which could provide some references for the design of future porous adsorbents.
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Contributions

All the authors have approved the final version of the manuscript.

Tao Xue Writing - original draft, Experiment, Research and investigation ideas.

Feifei Shao Investigation, Data curation. Han Miao Supervision, Writing - review & editing. Xinxin Li Conceptualization, Supervision, Project administration, first draft revision and final draft.

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Ethics declarations

Ethical approval
This research does not involve human participants and/or animals.

Consent to participate

All the authors have given their consent to participate.

Consent to publish

All the authors have given their consent to publish.

Competing interests

The authors have no relevant financial or non-financial interests to disclose.

Availability of data and materials

The authors confirm that the data supporting the findings of this study are available from the authors upon reasonable request.

Supplementary material

The following files are available free of charge.

Synthesis and structures of oleophilic Fe\textsubscript{3}O\textsubscript{4} nanoparticle; the scheme of the synthesis of porous magnetic adsorbents; the core-shell structures of hybrid nanoparticles; the compositions and structures of SY, RhB, and MB molecules; the equations of adsorption kinetic and its detail fitting dates; the adsorption equilibrium time of HSVF at 100 mg/L; the equations of adsorption isotherm and its detail fitting dates.
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